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Hydrothermal crystallization and electrical conductivity of aluminophosphate zeolites

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Abstract Synthesis of $AlPO_4$ zeolites has been carried out under hydrothermal conditions. The electrical conductivity has been determined for $AlPO_4$ zeolites, which contain mobile cations located in sites in cavities, on the channel walls, and free within the channels coordinated with water molecules. The electrical conductivity exhibited by zeolites is ionic and arises from the migration of cations through the zeolite framework. The thermodynamic parameters have been evaluated

Keywords Aluminophosphates ($AlPO_4$), zeolites, electrical conductivity

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1. Introduction

The aluminophosphate–based molecular sieve zeolites are synthesized by hydrothermal crystallization of reactive aluminophosphate gels containing the additional framework elements and an organic templates, at temperatures from 100°C to 250°C. The optimum crystallization temperature depends on composition and structure below 150°C. The pressure is generally autogeneous pressure approximately equivalent to saturated vapour pressure (svp) of water at the temperature designated. The conductivity measurement has been carried out for the $AlPO_4$ – zeolites.

2. Experimental methods

The general route whereby zeolites can be synthesized in a laboratory or a plant scale and schematic representation of zeolite synthesis is shown in Figure 1[1]. The structure directing agents listed are only examples of a wide range of materials that have been used. Zeolites have been synthesized only by hydrothermal method. The conditions generally used in synthesis are [2,3] :

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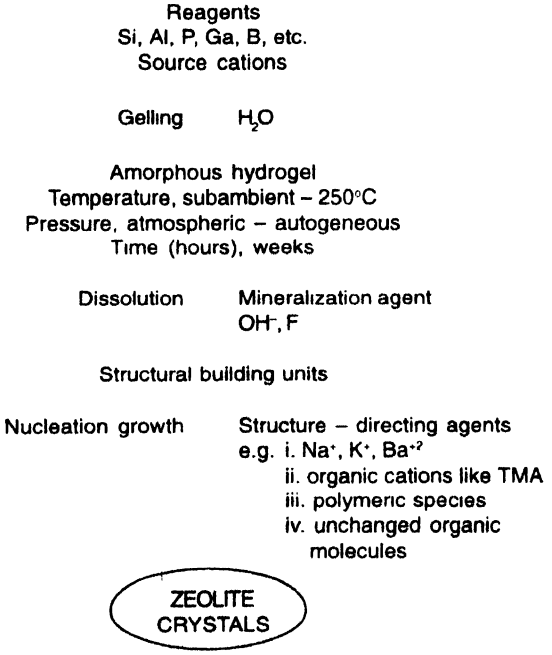

Figure 1. Schematic representation of zeolite syntheses

(a) Reactive starting materials such as freshly co-precipitated gels, or amorphous solids,

(b) relative high pH introduced in the form of an alkali metal hydroxide or other strong base,

(c) low temperature hydrothermal conditions with concurrent low autogeneous pressure at saturated water vapor pressure,

(d) a high degree of supersaturation of the components of the gel leading to the nucleation of a large number of crystals.

It involves silica, alumina and / or phosphorus species, metal cations, organic molecules as templates and water, which are converted *via* an alkaline supersaturated solution into a microporous crystalline zeolites. The complex chemical processes involved in this transformation can be denoted as zeolitization. The process of zeolitization is thermally activated and usually takes place at elevated temperature in order to achieve high yield of crystals in an acceptable period of time.

It is well known that the choice of source materials plays a crucial role in the synthesis and phase purity of aluminophosphate zeolites. Synthesis of aluminophosphate zeolites normally takes place by the following steps :

i) Neutralization of the Al – source suspended in water with nearly equimolar amount of dilute phosphoric acid to obtain the reactive aluminophosphate gel.

ii) Aging of the reactive gel.

iii) Addition of a particular organic additive to the reactive gel. This is referred to as precursor gel.

iv) Aging of the precursor gel, if necessary and finally

v) Closed hydrothermal treatment of the precursor gel

The time required for crystallization varies from a few hours to several days. A crystalline product is formed which is known as aluminophosphate zeolites. The electrical properties have been studied for these aluminophosphate zeolites.

The electrical conductivity of various forms of the synthetic zeolites was measured using polycrystalline compacts contained in a conductivity cell as illustrated in Figure 2 [4].

The conductivity data were obtained on aluminophosphate zeolites as a function of temperature at different concentration of Na^+ ions. Typical conductivity data for aluminophosphate zeolites are given in Figure 3, as arrhenius plots, conductivity σ versus 1/T. The activation energy for conduction, ΔH is shown in Figure 4, as a function of the Na^+ ion concentration. The

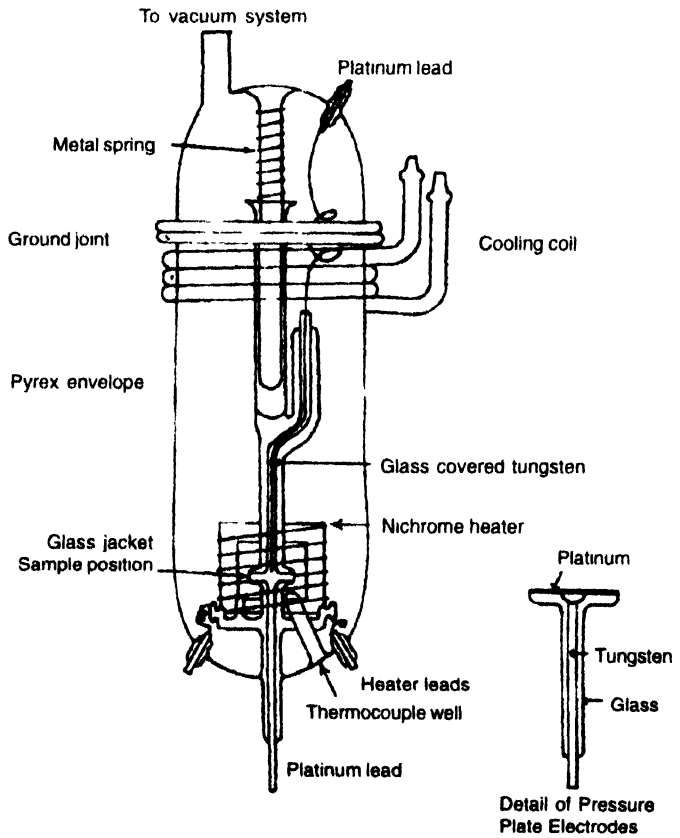

Figure 2. Cell for measuring conductivity of compacted, zeolite powder specimen.

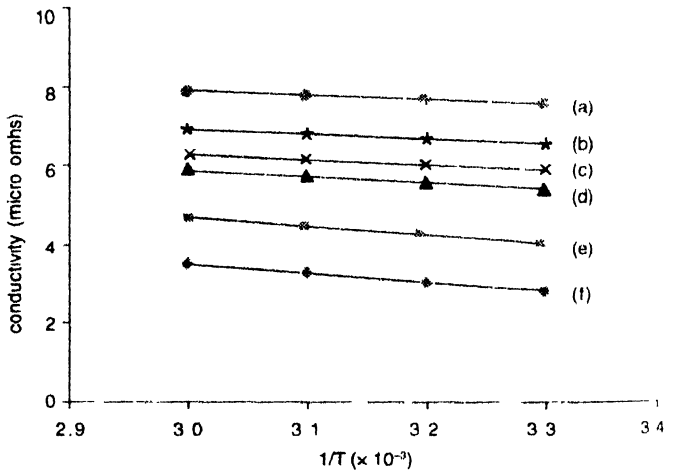

Figure 3. Arrhenius plots of electrical conductivity : (a) in 6% NaOH, (b) in 5% NaOH, (c) in 4% NaOH, (d) in 3% NaOH, (e) in 2% NaOH and (f) in 1% NaOH

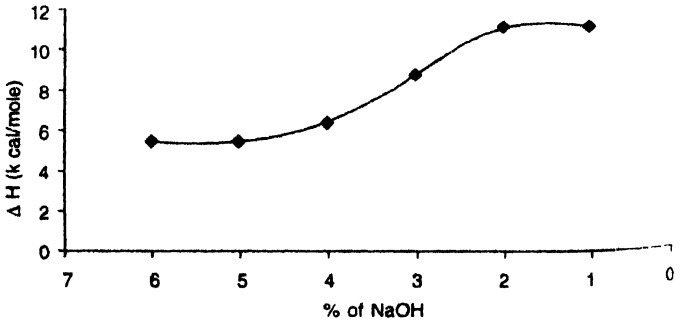

Figure 4. Variation of the activation energy with cation density in $AlPO_4$ – zeolites.

typical conductivity data for different concentration of aluminophosphate zeolite as a function of temperature at constant number of Na^+ ions were determined and activation energy, ΔH is obtained from arrhenius plots (Figure 5).

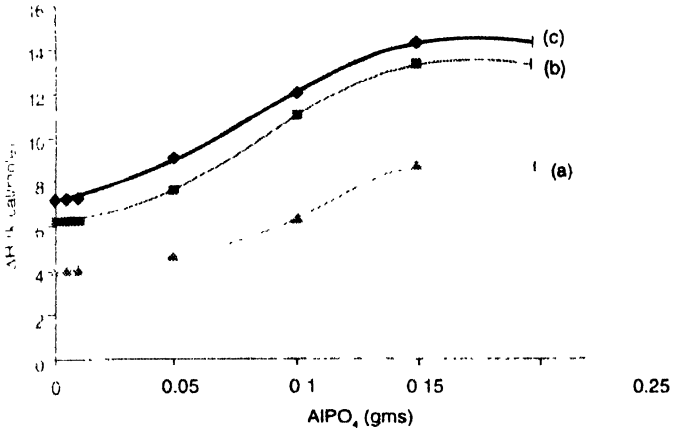

Figure 5. Variation of the activation energy with $AlPO_4$ – zeolites (a) in 6% NaOH, (b) in 3% NaOH and (c) in 1% NaOH

3. Results and discussion

The above results indicate that the conductivity was found to depend strongly on the cation mobilization in aluminophosphate zeolites. The increase of number of Na^+ ions at constant aluminophosphate zeolite concentration or decrease of concentration of aluminophosphate zeolite at constant Na^+ ions, decreases the cation density in the aluminophosphate zeolite. The activation energy, ΔH increases rapidly starting for 0.05 gms of aluminophosphate zeolite or Al/P ratio of 1.5. This indicates two types of cation sites. Further, the activation energy ΔH increases as the cation density decreases in aluminophosphate zeolite which is a characteristic of more strongly bound cation.

The conductivity was found to depend strongly on the cation size and the size of the channels within the zeolite structure. The activation energy ΔH decreases due to a diminishing Coulombic attraction between the cation and cation site. The addition of OH^- molecules to the aluminophosphate zeolite structure produce a pronounced change in the electrical conductivity. The conductivity increases linearly. This reflects the preferential hydration of one type of cation in the structure. The conductivity increases as the crystals become saturated, indicating that the channel systems are filled. Some of the Na^+ ions are free to move randomly within the channels.

4. Conclusions

The conduction mechanism includes a frequency dependent process ascribed to motion of cations in the super cages over a range of energy barriers. Assuming that the conduction process involves only cation located in the super cages, ions located on site II would have to migrate over a sequence of three 4-rings to reach another surface site II. The difference in the activation energy for conduction has been attributed to the presence of cations in the weakly bound sites or to difference in the electrostatic interaction between cations and the oxygen frame work.

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